PERCHLORATE REMOVAL FROM WATERS
BY MEMBRANE-IMMOBILIZED BIOFILM

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Introduction

Perchlorate has been found in surface and ground waters in the western states of America recently. Perchlorate is a health concern due to its interference with iodine in the production of hormones in the thyroid. Perchlorate is difficult to be chemically or physically removed, so the conventional water treatment technologies, such as air stripping, and adsorption, have no effect on perchlorate removal or destruction. However, perchlorate is very biodegradable. Several biological treatment systems are currently under investigation to remove perchlorate from water so that it can be subsequently used as a source of drinking water. These treatment systems include anoxic fluidized bed methanol-fed reactor, sand filter bed, and hydrogen gas-phase reactor. A disadvantage of the above systems is that bacteria used to degrade the perchlorate will come directly into contact with the water being treated. A membrane-immobilized biofilm system can separate the perchlorate contaminated water from the microbes, greatly minimizing the presence of microbes in the finished water. Biofilms, capable of perchlorate biodegradation, can be quickly developed on membrane surfaces. This research investigates the design parameters of a membrane-immobilized biofilm reactor to remove perchlorate from waters.

Development of Perchlorate Degrading Enrichment Cultures & Kinetics

A perchlorate degrading enrichment culture was developed from the returned activated sludge (RAS) from the Clark County Sanitation District (CCSD) wastewater treatment plant in Las Vegas. The culture was enriched by adding perchlorate, nutrient/minerals, buffer and carbon source to the mixed liquor and incubating it at 22°C. After a large period of incubation, red color microorganisms were observed in the reactor. The culture was named BALI (for BAtista and LIu).

Preliminary kinetics studies were performed in the enrichment "BALI" culture. The objectives of these experiments were to determine the limiting carbon to perchlorate ratios needed for perchlorate biodegradation by this culture. One set of tests was performed under perchlorate limited condition while the other set was performed under carbon (lactate) limited condition. In the perchlorate limited tests, the lactate concentration was 1,000 mg/L and perchlorate concentrations varied from 10 to 200 mg/L. For the lactate limited tests, the perchlorate concentration was constant and equal to 100 mg/L; lactate concentrations varied from 20 to 300 mg/L. The tests were performed in 125-ml serum bottles in duplicate. The desired amounts of perchlorate, lactate, buffer and nutrient/minerals were added to the individual bottles. The same amount of microbes ("BALI") from the master reactor, for which the total suspended solids concentration was known, was added to each bottle so to obtain a suspended solids (SS) concentration of approximately 3.5 mg/L.

The results indicate that a larger acclimation time (3 days) was needed for the bottles containing the highest perchlorate concentrations (100 and 200 mg/L). For the bottles containing lower perchlorate concentrations (10-60 mg/l) only about 2 days were required for complete biodegradation (Figure 1). Figure 2 shows that perchlorate and lactate were biodegraded by the microorganisms, their concentrations decreased with time, while the concentration of chloride, the final product of perchlorate biodegradation, increased with the time. The results also indicate that a lactate to perchlorate ratio of at least three is needed for perchlorate biodegradation to occur (Figure 3).
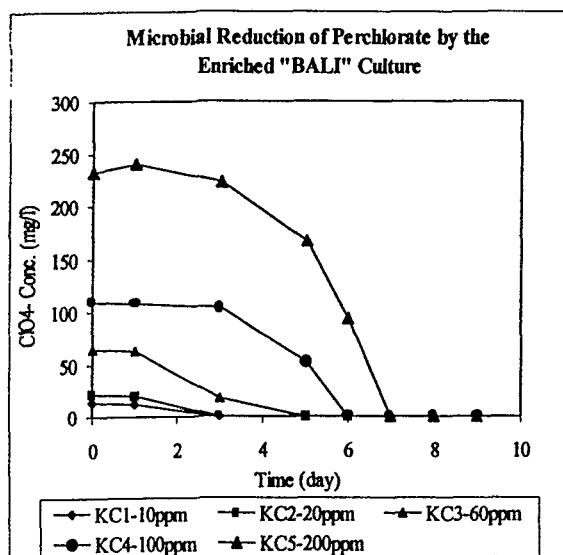

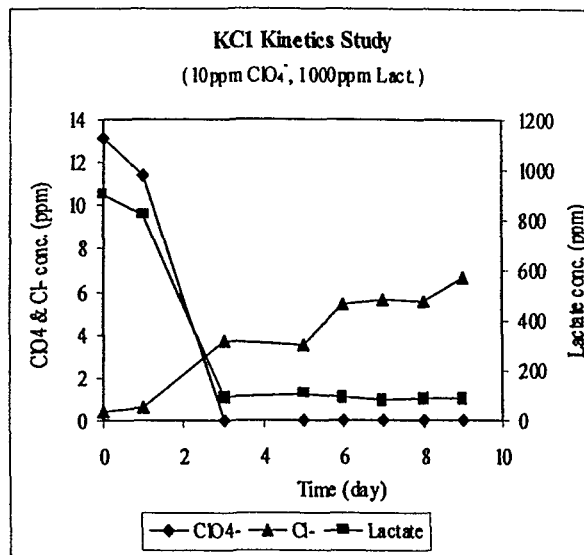Figure 1: Perchlorate Biodegradation in Perchlorate Limited Bottles

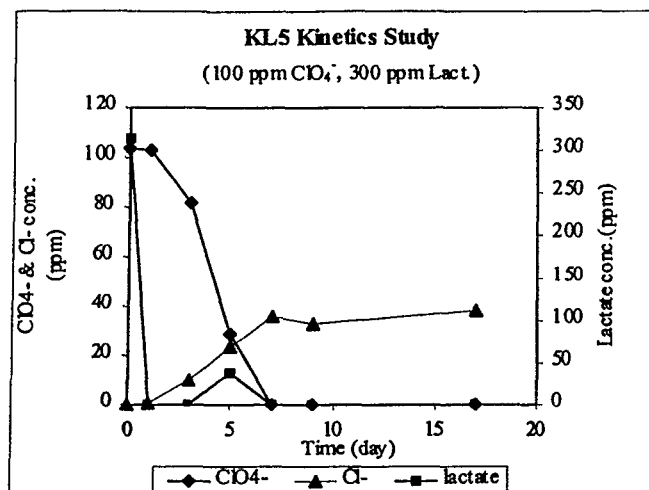Figure 2:Microbial reduction of perchlorate to chloride when lact./ClO_4^-=100

KL5 Kinetics Study
(100 ppm ClO_4^-, 300 ppm Lact.)

Figure 3: Microbial reduction of perchlorate to chloride when lact./ClO_4 =3

Membrane Diffusivity Testing

Three perchlorate resistant membranes were chosen as potential candidates for the immobilization of a biofilm for perchlorate biodegradation. The diffusivity of perchlorate through these membranes, prior to biofilm growth, was determined experimentally to evaluate the migration of perchlorate from the diffusion reactor (DR; left side) to the biofilm reactor (BR; right side) (Figure 4). The selected membranes were Memcor BTS-55, Memcor PVDF, and Millipore FGLP membrane. All three types of membranes were tested in duplicate. The diffusion coefficient was determined by placing a circular piece of membrane (10 cm diameter) between the two tanks. The diffusion chamber was then filled with 5 liters of DI water containing 1000 mg/L perchlorate. The perchlorate concentration on the biofilm reactor was monitored every 15 minutes.
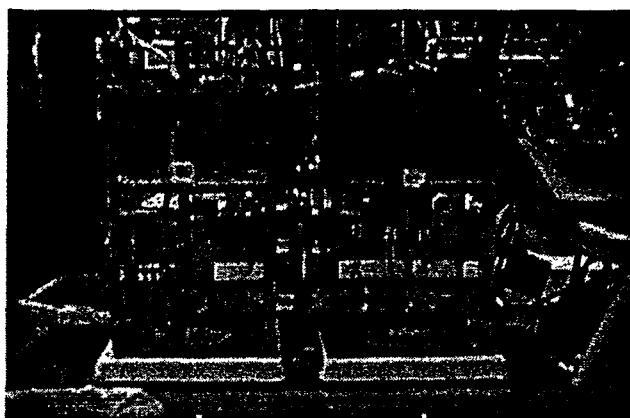

Figure 4: Perchlorate Diffusivity Testing Through Microporous Membranes

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Diffusivity was calculated by using Fick's law:

$$V_{BR}\,(\partial C_{BR}/\partial t) = -\,(D_M A_M)/(\Delta L_M)(C_{DR}-C_{BR})$$

Where C_{DR0} is the initial concentration of perchlorate in diffusion chamber, C_{DR} is the concentration of perchlorate in the diffusion chamber at time t, and C_{BR} is the concentration of perchlorate in the biofilm chamber. Since the two chambers contained the same volume of water that $C_{DR} = C_{DR0} - C_{BR}$. The integration of the above differential equation yields:

$$\mathrm{Ln}\,[(C_{DR0} - 2C_{BR})/(C_{DR0} - 2C_{BR0})] = -\,(2A_M D_M t)/(V_{BR}\Delta L_M)$$

Where V_2 is the volume of one chamber, A_M is the membrane pore area $= \pi r^2 \varepsilon (cm^2)$, ΔL_M=membrane thickness (cm), r = filter radius (cm), ε=mean pore fraction (0.7 for all membrane tested), D_M=perchlorate diffusivity coefficient through the membrane (cm^2/s), and t=elapsed time (s). The diffusivity was determined by least-square regression of the transformed experimental data.

Result of Perchlorate Diffusivity Tests Through Membranes

As shown in Figure 5, for the BT-55 membrane both tests had R^2 values greater than 0.99 and the same slope of −0.0007. The calculated diffusion coefficient is therefore 6.64×10^{-6} cm^2/sec. For the PVDF membrane, some variability was found in the duplicate tests. Both R^2 values were greater than 0.99, but the slopes were different and equal to -0.0004 and -0.0006 for tests 1 and 2, respectively. The calculated diffusion coefficient based on test 1 was 3.0×10^{-6} and 4.5×10^{-6} cm^2/sec for test 2. The average diffusion coefficient for this membrane is then 3.75×10^{-6} cm^2/sec. The FGLP membrane data for both tests were very similar with R^2 values greater than 0.97. The slope was the same for both tests and a diffusion coefficient of 6.67×10^{-6} cm^2/sec was calculated.

For comparison, the diffusivity of perchlorate in water, without a membrane, was calculated by using the Wilke-Chang Method, in which the molar volume of perchlorate was calculated using the Method of LeBas. The diffusion coefficient of perchlorate calculated by the Wilke-Chang method (Reid, 1987) was found to be 1.53×10^{-5} cm^2/sec . Therefore, the diffusivity of perchlorate through the microporous membranes tested is significantly smaller than that in water. This result confirms the hypothesis that perchlorate would migrate through semipermeable membrane by diffusion. The diffusivity of perchlorate through all three membranes was evaluated. The membrane characteristics as well as the calculated diffusion coefficients are summarized in Table I.

Table I Experimental Determination of Perchlorate's Diffusion Coefficient Through Different Types of Membranes			
Membrane Type	Memcor BTS-55	Memcor PVDF	Millipore FGLP
Pore Size, μm	0.2	0.45	0.2
Thickness, μm	125	99	220
Pore Fraction, %	70	70	70
Diffusion Coefficient, cm^2/sec (testing)	6.64×10^{-6}	3.75×10^{-6}	6.67×10^{-6}
Diffusion Coefficient, cm^2/sec (Wilke-Chang Method)		1.53×10^{-5}	

Perchlorate Diffusion Coefficient Through
Memcor BTS-55 Membrane
0.2 Microns Diameter

Test 1
$y = -0.0007x + 0.0019$
$R^2 = 0.9941$

Test 2
$y = -0.0007x + 0.0031$
$R^2 = 0.9937$

Y-axis: Ln[(CB0-2CA)/(CB0-2CA0)]

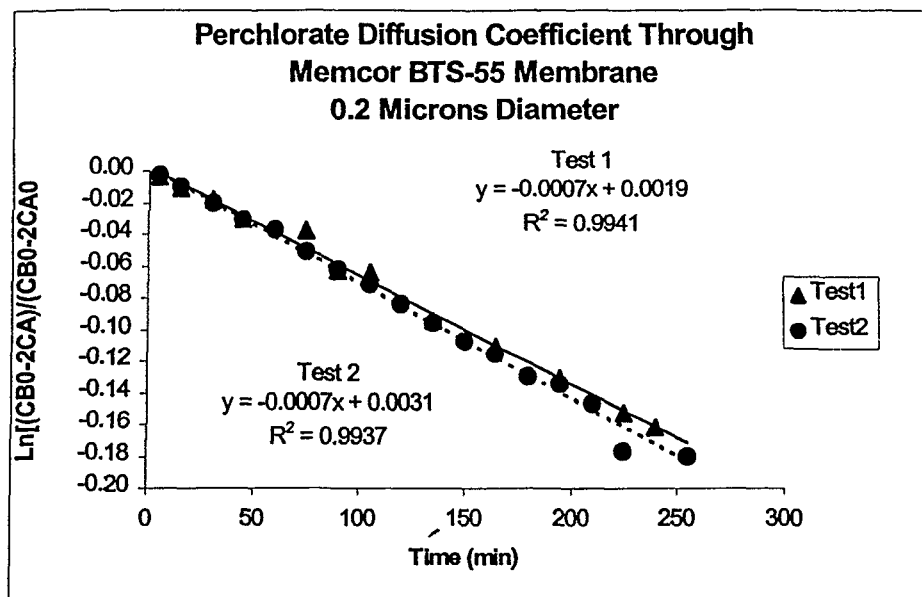X-axis: Time (min)

Legend: ▲ Test1 ● Test2

Figure 5: Perchlorate Diffusion through Memcor BTS-55 Membrane

Development of Membrane Immobilized Biofilm

To investigate the biodegradation of perchlorate by an immobilized biofilm, it is necessary to first establish a biofilm on the surface of the membrane. A membrane was placed between the two reactors. The biofilm was established on the BR reactor over a week period prior to the experiments. Two sets of reactors (4 tanks) were available to facilitate concomitant biofilm growth and biodegradation studies. Five liters of DI water containing 1000 mg/L lactate, 200 mg/l perchlorate (lactate/perchlorate ratio of 5:1), nutrients/minerals and buffer solutions and seed microbes (0.1 g/L) from the master reactor were added to the BR reactor. Five liters of DI water were also added to the DR reactor to keep the hydraulic pressure on both sides of the membrane the same. A YSI 54A oxygen meter and a Corning pH/Ion meter 450 was placed in the BR to continuously control the oxygen concentration and the pH. Deoxygenation in the BR reactor was obtained and kept by stripping with nitrogen gas using fine-bubble ceramic diffusing stones. Oxygen levels were kept undetectable at all times. Biofilm growth was observed not only in the membrane, but also in the walls of the tank, However, given the hydraulics of the reactor, a thicker biofilm developed in the membrane than in the walls of the tank.

Perchlorate Biodegradation by the immobilized Biofilm

Biofilms were developed in all three selected microporous membrane and perchlorate biodegradation by the membrane-immobilized biofilm was investigated. After establishment of the biofilm in the BR reactor side of the membrane. Five liters of solution containing lactate, nutrients/minerals and buffer were then added to the BR reactor. Five liters of solution

containing perchlorate was added to the DR reactor on the other side of the biofilm. The concentrations of perchlorate, lactate, chloride, and suspended solids were monitored in both the BR and the DR reactors. One cycle consists of a run from an initial perchlorate concentration to a lower desired perchlorate level in the DR reactor.

Results of Perchlorate Biodegradation Testing

Three testing cycles were performed by the BTS-55 membrane-immobilized biofilm (Figures 6, 7, and 8). Figures 6 shows that after 5 days, all perchlorate diffused to the BR reactor was biodegraded. The concentration of perchlorate in the BR reactor, at all times, was very small. The lactate in the BR reactor decreased proportionally to perchlorate in the DR reactor. However, lactate kept decreasing although no more perchlorate was available. It is suspected that lactate was fermented, since the work is being performed using a mixed culture. Figure 6 also shows that contrary to perchlorate and lactate, chloride concentration changes significantly from one reactor to another. This is due to two factors: (a) diffusion of chloride through the membrane due to its small size, (b) movement of water from the DR reactor (smaller concentration of ions) to the BR reactor (highef concentration of ions) by osmotic pressure. In all the tests performed with this membrane, migration of water from the DR to the BR reactor was observed. That means, with time, the volume of water in BR increased. The chloride concentration stabilizes when both reactors contain about the same concentration of chloride. The fact that water is transferred by osmotic pressure to the BR reactor may has implications in the design of full-scale membrane-immobilized biofilm reactors for product water (perchlorate free) could migrate to the BR reactor, decreasing the total volume of treated water produced. The results of the 1st cycle of perchlorate biodegradation through BTS-55 membrane-immobilized biofilm show: (1) the molar ratio of perchlorate biodegraded to that of chloride formed to be 0.82 for this run. Theoretically, each mole of perchlorate would generate one mole of chloride, thus this ratio is somewhat smaller than expected. (2) about 1.95 moles of perchlorate were biodegraded by the biofilm per day. For this calculation only the first six days of the experiment were considered, since the system was perchlorate-limited after the sixth day.

For the second and third cycles, more lactate, nutrient, and buffer were added to BR reactor and more perchlorate was added to the DR reactor. The addition was made to the resulting solutions from the previous cycles. The high chloride concentrations in the first day are the result of the perchlorate biodegradation from the previous cycles. As can be seen in Figures 7 and 8, perchlorate was easily biodegraded by the biofilm as indicated by the decrease in perchlorate concentration and the increase in chloride concentration. Perchlorate degradation in the second cycle (0.90 moles ClO_4^- per day) was slower than in the first cycle (1.95 moles ClO_4^- per day) and third cycles (1.75 moles ClO_4^- per day). Possible reasons for the difference in degradation rates in the three cycles include: (a) difference in biofilm thickness. It is not possible to measure the thickness of the biofilm between cycles, without terminating the experiment, but visually the biofilm seems thicker with time. (b) change in the microbial ecology of the reactor due to lactate degradation in the absence of perchlorate. In several runs, it was observed that when perchlorate was absent, lactate degradation still proceeded. As mentioned above, in the first cycle perchlorate biodegraded at a rate of 1.95 moles/day. After the fifth day, all perchlorate was degraded , but lactate biodegradation proceeded for ten more days. In the second cycle,

perchlorate biodegradation rate was only 0.90 moles/day, but in cycle three, the perchlorate biodegradation was 1.75 moles/day, similar to that of the first cycle. It is possible that fermentation occurred at the end of the first cycle, negatively affecting perchlorate biodegradation in the second cycle. This observation deserves further investigation for it would be of interest to the operation of full-scale plants, to determine whether the capacity of microbes to biodegrade perchlorate is decreased, when fermentation occurs at very low perchlorate and high lactate concentrations.
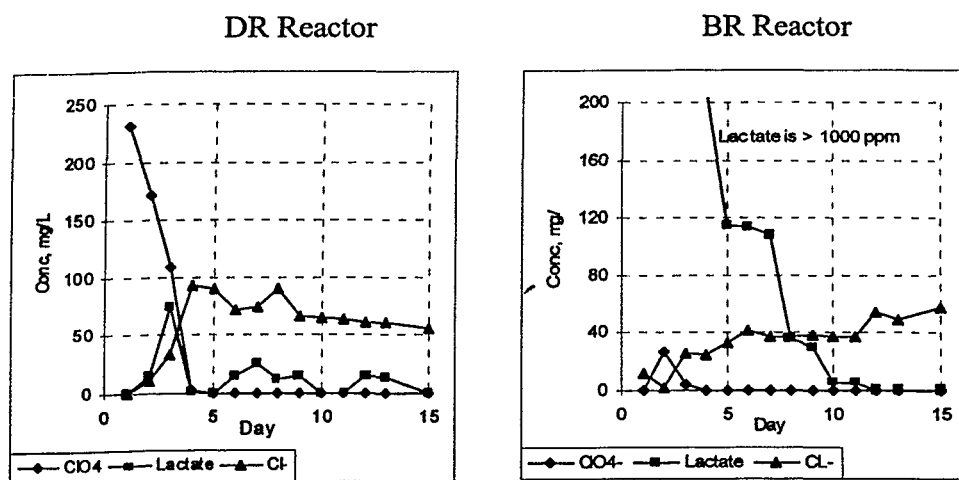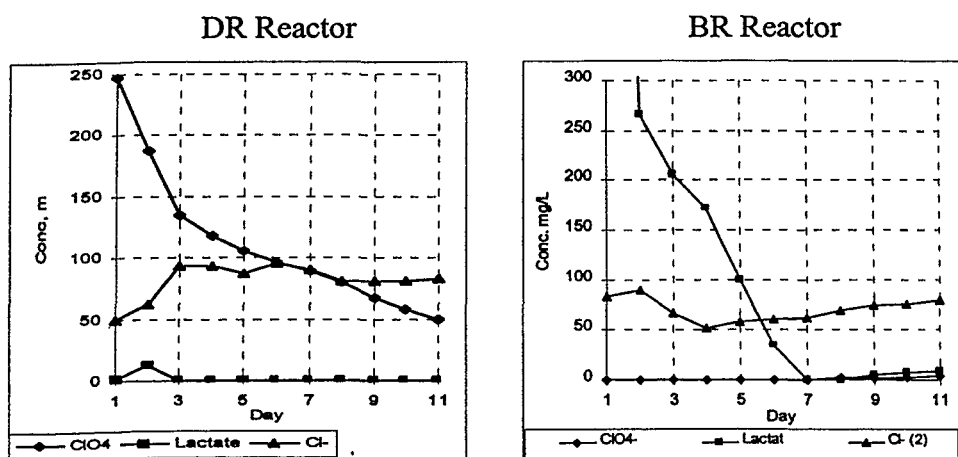

Figure 6:   Perchlorate, lactate, and chloride concentrations in the DR, and BR reactors during biodegradation of perchlorate by a biofilm immobilized on a BTS-55 Membrane (1st Cycle)

$ClO_4^- / Cl^- = 0.82$; ClO_4^- biodegradation rate = 1.95 moles/day

Figure 7:   Perchlorate, lactate, and chloride concentrations in the DR and BR reactors during biodegradation of perchlorate by a biofilm immobilized on a BTS-55 Membrane (2nd Cycle)

$ClO_4^- / Cl^- = 1.03$; ClO_4^- biodegradation rate = 0.90 moles/day
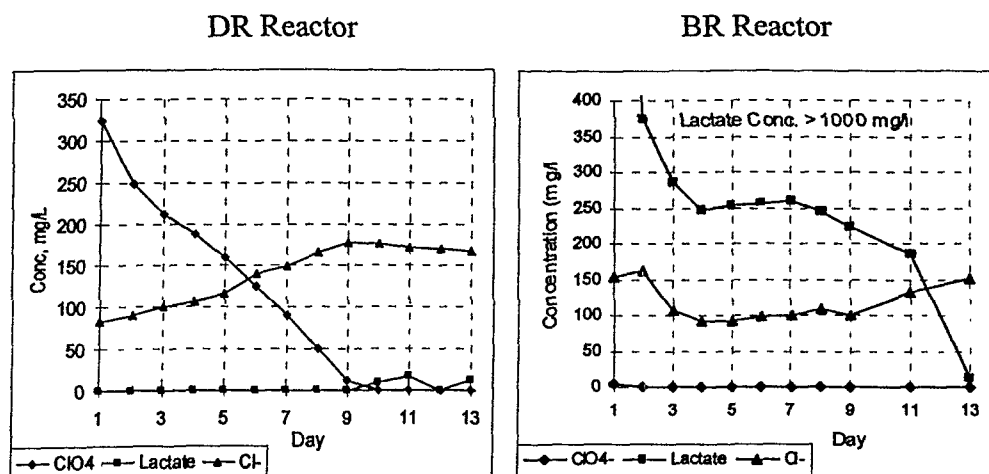
Figure 8:   Perchlorate, lactate, and chloride concentrations in the DR and BR reactors during biodegradation of perchlorate by a biofilm immobilized on a BTS-55 Membrane (3rd Cycle)

$ClO_4^- / Cl^- = 0.86$; ClO_4^- biodegradation rate = 1.75 moles/day

Two biodegradation cycles were run for the perchlorate biodegradation through the FGLP membrane-immobilized biofilm. In the first cycle, 223 mg/L perchlorate was added to the DR reactor separated by a biofilm immobilized on Millipore FGLP membrane. In the BR reactor 1100 mg/l lactate, nutrients/minerals and buffer were added. Notice that in nine days only about 37 mg/L was biodegraded. Perchlorate diffusion was very poor through the biofilm immobilized in this membrane. This was unexpected, since this membrane showed the largest diffusion coefficient in the diffusion tests without a biofilm. It is worth mentioning that the biofilm developed in this membrane was very thick. This happened because this membrane has a plastic backing that favors microbial attachment. Therefore, transport of perchlorate to the BR reactor was limited by diffusion. Also notice that the chloride concentration in the BR and in the DR reactors increased with time, indicating perchlorate biodegradation. (Figure 9) The results show that chloride migrated easily from the BR to the DR reactor with time, due to its small molar volume. Although only a small amount of perchlorate was biodegraded, a large amount of lactate was used in the BR reactor. Since the work is being performed using a mixed- biological culture, it is likely that lactate was used as a carbon source by microbes in the biofilm which are not dependent on perchlorate as an electron acceptor.

In a second trial with the FGLP membrane, 223.16 mg/L perchlorate were added to the DR reactor and 1099.8 mg/l lactate, nutrient and buffer were added to the BR reactor. As shown in Figures 10, only very small amounts of perchlorate were able to diffuse to the BR reactor and biodegradation of perchlorate was again limited by diffusion through the thick biofilm. It is concluded from the above results that the FGLP membrane is not suitable for the thought purpose.

DR Reactor   BR Reactor
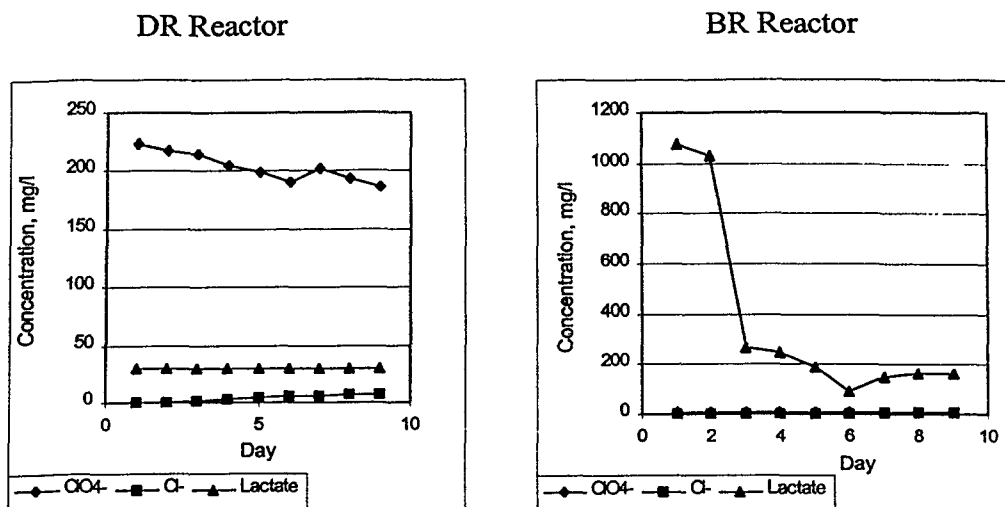

Figure 9:   Perchlorate, lactate, and chloride concentrations in the DR and BR
             reactors during biodegradation of perchlorate by a biofilm immobilized
             on a FGLP Membrane (1st Cycle)

DR Reactor   BR Reactor
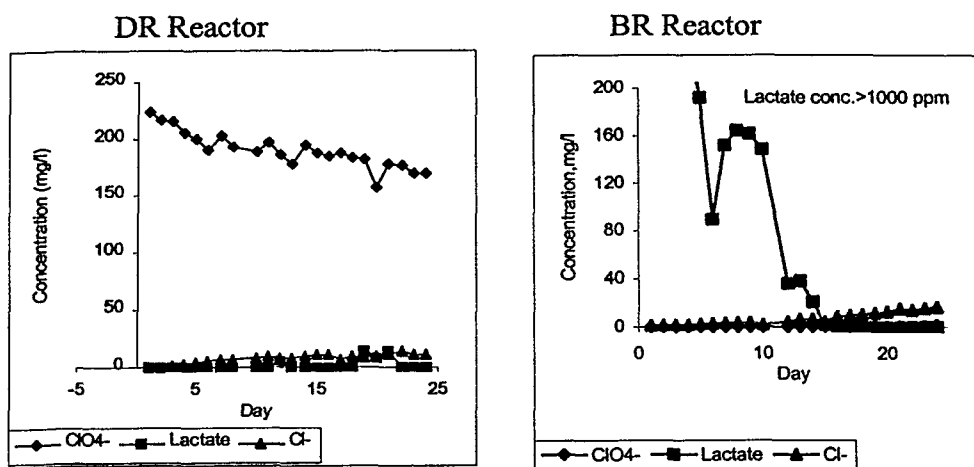

Figure 10: Perchlorate, lactate, and chloride concentrations in the DR and BR reactors
           during biodegradation of perchlorate by a biofilm immobilized on a FGLP
           Membrane (2nd Cycle)

One biodegradation cycle was also run with a biofilm grown on the PVDF membrane. The
results of the perchlorate biodegradation through biofilms immobilized on two types of
membranes are shown in Table II. As seen in Table II, the BTS-55 membrane works better for
the purpose.

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Testing Cycle and	Membrane Type	
	BTS-55	PVDF
First Cycle	ClO_4^- / Cl^-: 0.82	ClO_4^- / Cl^-: 0.99
Second Cycle	ClO_4^- / Cl^-: 1.03	
Third Cycle	ClO_4^- / Cl^-: 0.86	
First Cycle	Moles ClO_4^-/day: 1.95	Moles ClO_4^-/day: 0.5
Second Cycle	Moles ClO_4^-/day: 0.90	
Third Cycle	Moles ClO_4^-/day: 1.75	

Table II   Summary of Relevant Parameters Calculated for the Biofilms Immobilized on the BTS-55 and PVDF Membranes

Conclusion

- Perchlorate easily migrates through semipermeable membranes by diffusion, eliminating the need of energy input. The diffusivity of perchlorate through the microporous membranes tested is significantly smaller than that of perchlorate in water.

- Kinetics study of "BALI" indicates that a lactate to perchlorate ratio of at least three is needed for perchlorate biodegradation to occur, and acclimation time varies with the concentrations of perchlorate.

- Biofilms, capable of perchlorate biodegradation, can be quickly developed on the membrane surface.

- Perchlorate biodegradation by the membrane-immobilized biofilm was found to be fast and steady. The testing indicates that a membrane-immobilized biofilm is a very good reactor set-up for perchlorate biodegradation. The existence of the membrane allows for controlled diffusion of perchlorate to the BR reactor, so that the concentration of perchlorate in the finished water can be kept at a desired level without fluctuations or sporadic spikes. In addition, the amount of microbes in the product water is very small, given the contaminated water is isolated from the microbes by the membrane. For the treatment of contaminated drinking water this reactor set-up is very promising.

- When a carbon source (lactate) is added to the BR reactor, perchlorate quickly degrades to chloride. Calculated ratios of perchlorate to chloride are very close to the theoretical ratios.

- Scale up configuration for the reactor will involve elongated channels separated by one membrane or membrane sandwiches.

- The final reactor design will depend on the experimental data collected from the interference of other anions on perchlorate biodegradation and diffusion to be performed in the second year of the research.